U.S. DEPARTMENT OF COMMERCE
National Technical Information Service
PB80-124480

Application of an Electrostatic Precipitator for Instrumental Sampling of Sulfuric Acid

(U.S.) Environmental Sciences Research Lab,
Research Triangle Park, NC

23 Mar 79

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	3. RECIPIENT'S ACCESSION NO.
EPA-600/J-79-044	JOURNAL ARTICLE	PB80-124480

4. TITLE AND SUBTITLE
APPLICATION OF AN ELECTROSTATIC PRECIPITATOR FOR INSTRUMENTAL SAMPLING OF SULFURIC ACID

5. REPORT DATE

6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S)
Cheney, J. L., Walters, C. L., and Homolya, J. B.

8. PERFORMING ORGANIZATION REPORT NO.

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Same as No. 12.

10. PROGRAM ELEMENT NO.
1AD712B BA-020 (FY-79)

11. CONTRACT/GRANT NO.

12. SPONSORING AGENCY NAME AND ADDRESS
Environmental Sciences Research Laboratory - RTP, NC
Office of Research and Development
U.S. Environmental Protection Agency
Research Triangle Park, N.C. 27711

13. TYPE OF REPORT AND PERIOD COVERED

14. SPONSORING AGENCY CODE
EPA-600/09

15. SUPPLEMENTARY NOTES
REFERENCE: Analytical Letters, 12(A7):783-801,1979.

16. ABSTRACT

A means of separating gaseous sulfuric acid from flue gas particles has been evaluated. Previous attempts to achieve separation by filtration resulted in retention of the acid by the particulate buildup on the filter surface. A laboratory study of a prototype electrostatic precipitator, followed by actual flue gas sampling, indicated that the precipitator may eliminate the need for a filter without affecting the measurement results. The study also showed that the precipitator could be used preceding a prototype acid monitor for the continual monitoring of H_2SO_4 in combustion gases.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
* Air pollution		13B
* Sulfuric acid		07B
* Particles		13I
* Electrostatic precipitators		

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS *(This Report)*	21. NO. OF PAGES
RELEASE TO PUBLIC	UNCLASSIFIED	21
	20. SECURITY CLASS *(This page)*	22. PRICE
	UNCLASSIFIED	A02 A01

ANALYTICAL LETTERS, 12(A7), 783-801 (1979)

EPA-600/J-79-044
JOURNAL ARTICLE

APPLICATION OF AN ELECTROSTATIC PRECIPITATOR FOR INSTRUMENTAL SAMPLING OF SULFURIC ACID

KEY WORDS: Sulfuric acid, flue gas sampling, electrostatic precipitator, particulate removal

J. L. Cheney, C. L. Walters, and J. B. Homolya

Gaseous Emissions Research Section
Environmental Sciences Research Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, N.C. 27711

ABSTRACT

A means of separating gaseous sulfuric acid from flue gas particles has been evaluated. Previous attempts to achieve this separation by filtration resulted in retention of the acid by the particulate buildup on the filter surface. By conducting a laboratory study of a prototype electrostatic precipitator, followed by actual flue gas sampling, it was found that the precipitator may eliminate the need for a filter without affecting the measurement results. It was also found that the precipitator

could be used prior to a prototype acid monitor for the successful continual monitoring of H_2SO_4 in combustion gases.

INTRODUCTION

The direct measurement of gaseous sulfuric acid emissions from fossil fuel combustion sources has been difficult due to the presence of particulate matter. During corrosion studies in the past, it was procedural to filter out the particles, with either glass or quartz wool inserted in the probe tip of the extractive sampling apparatus. The H_2SO_4 was collected subsequent to the probe, either by absorption[1] or condensation[2]. While considerable debate evolved concerning the acid collecting approaches, little concern was expressed over the passage of H_2SO_4 through the filter. Consequently, it was routine to discard the probe plug, as it was considered to contain only inorganic sulfate.

More recent work[3] involving sulfate measurements has indicated some serious problems by such a filtration approach. These problems result from the reaction of gaseous H_2SO_4 with filtered particles, either reversible or irreversible[4]. Among the many variables which can affect the extent to which such reactions might occur are: temperature, acid and particle concentration, and physical and chemical characteristics of the particles. These variables are continuously changing, even for a given combustion system due to changing excess air, particle buildup on the combustion system surface, and boiler load variation. The extent of the reactions is even more influenced

by fuel composition when, for example, comparing oil to coal or hogged-fuel. The extent of the reaction of H_2SO_4 with particles is most dramatic at the interface of the sample and the particulate buildup on the filter. The buildup of ash on the filter enhances any potential gas-solid reaction with the subsequent gas phase portion of the sample. High temperature and flow rate have been found[5] to minimize this reaction. It has also been found that minimizing the sample volume results in a corresponding decrease in the reaction[6].

Our most recent efforts to measure H_2SO_4 in combustion gases involve continual measurement with a prototype monitor[7]. Because this instrument measures H_2SO_4 by a conductivity reading, particulate matter must be removed from the sample gas stream. The length of time the automatic measurements could be taken, however, was greatly curtailed by the limited volume a given filter could tolerate for complete particle removal while retaining a minimum amount of H_2SO_4. Using the same type of high temperature filtration as in a similar manual method[8], a 1 hr maximum sampling period with the instrument has been experienced, followed by a time consuming change in filter media.

This work involves the preliminary evaluation of a prototype electrostatic precipitator (ESP). The Drinker[9] type precipitator, which theoretically would remove particles from the combustion gas without filtration, would minimize the interaction of H_2SO_4 and particles. Using the prototype ESP, a high temperature quartz filter and a prototype acid monitor, studies were performed to determine the effect the ESP would have on quartz filter lifetime, sulfate distribution in the ESP and filter, as well as any effect the ESP would have

on instrument signal. This evaluation was done first on a brief laboratory bases, followed by field use of the ESP as part of the sample handling apparatus during continual H_2SO_4 monitoring.

EXPERIMENTAL

H_2SO_4 sampling was conducted at a local 100,000 lb./hr. oil-fired steam boiler, using both a total water soluble sulfate (TWSS) manual method[3] as well as a prototype acid monitor. As full details of the instrument have been provided[7] elsewhere, it will be discussed here only briefly. Figure 1 shows the automated sampling, sample recovery, and measurement schematics the monitor utilizes. Being a fully automatic method, the operator needs only to replenish reagents periodically under normal use. The monitor utilizes the selective condensation[8] measurement approach, the water jacketed glassware of which is shown in Figure 2. After condensation of the H_2SO_4, which follows sample filtration, a premeasured volume of 95% isopropanol/H_2O washes the collected acid into the conductivity cell. During this work, the water bath, and hence the glassware, was maintained near 60°C.

The manual sampling method used for this work was the Modified EPA Method 6 for measuring total water soluble sulfates (TWSS). This method provides a measure of sulfur dioxide (SO_2) as well as total sulfate. During some of the studies using the monitor, a Greenburg-Smith impinger containing 10% hydrogen peroxide was used after the monitor to provide an additional SO_2 measurement (shown as optional in

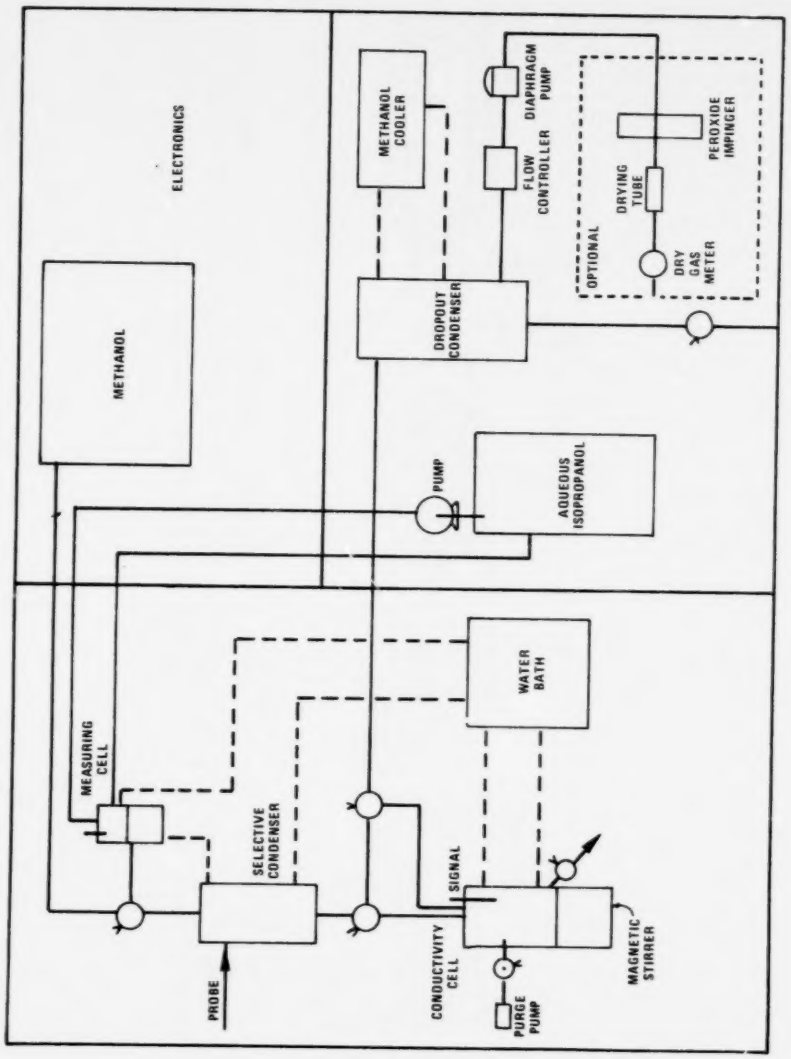

Figure 1. Flow schematics of acid monitor.

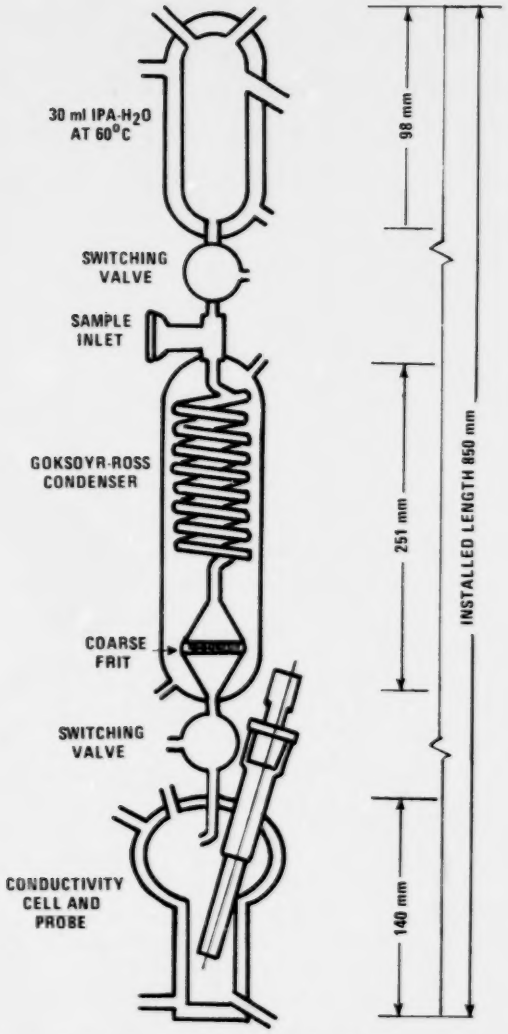

Figure 2. Water jacketed glassware for H_2SO_4 monitor.

Figure 1). In addition, it was felt necessary on occasion to recover the contents of the conductivity cell. The recovered conductivity cell contents as well as all other collected samples were titrated using the Barium-Thorin procedure described in the TWSS method.

Flow characteristics, which can be preset within the instrument with a mass flow controller, were confirmed using the optional dry gas meter and a stopwatch.

The flue gas sample handling apparatus consisted of a high temperature quartz probe, a high temperature prototype electrostatic precipitator, and a high temperature quartz filter and filter holder. The prototype ESP (Figure 3), was designed to collect particles from a flue gas with a grain loading of 0.02 grains/dry standard cubic feet (g/dscf) for a total sample volume of $12m^3$. Just subsequent to the ESP is the quartz filter holder, which is heated along with the ESP as a unit. In order to maintain temperature control, a thermocouple was contained under the heating tape near the filter holder.

Shown in Figure 4 are the schematics of the electronic power supply pack along with its chassis case. The power supply allows application of 0 to 16 Kilovolts across the ESP electrodes. This crdinarily results in a current flow of from 0 to 50 μ amps; however, the current fluctuates somewhat as the particles accumulate during sampling.

The preliminary collection efficiency study of the ESP was performed in the laboratory using ambient air both with and without the precipitator preceding a particle counter. The amount of particle breakthrough from the ESP was measured with a Climet, Model 208 Par-

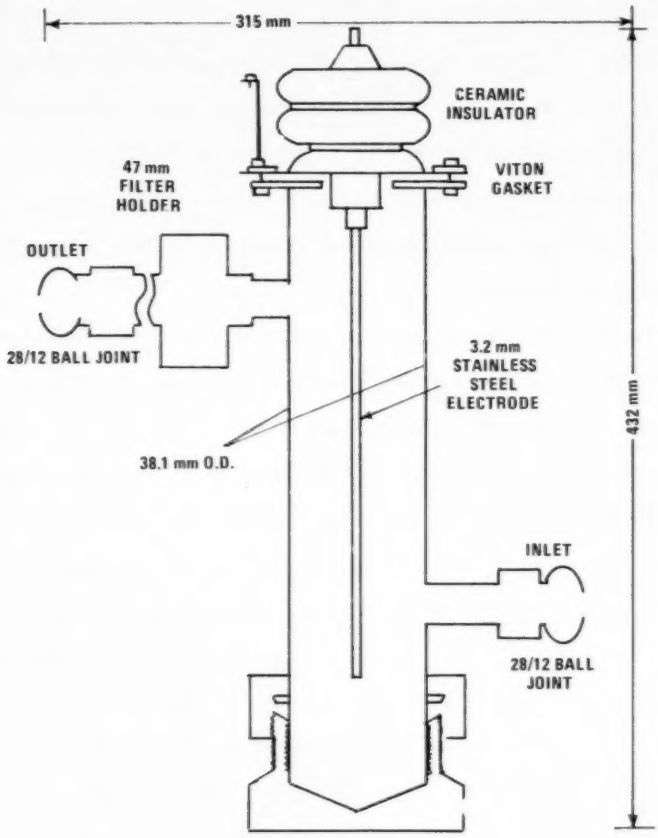

Figure 3. Description of prototype electrostatic precipitator.

ticle Counter. During the actual flue gas sampling, the ESP was maintained at 40 to 50 μa.

During sample recovery of H_2SO_4 and sulfate from the probe, ESP, and filter, the acid was recovered by first washing the component with 100% isopropanol, and filtering. Following this the component was

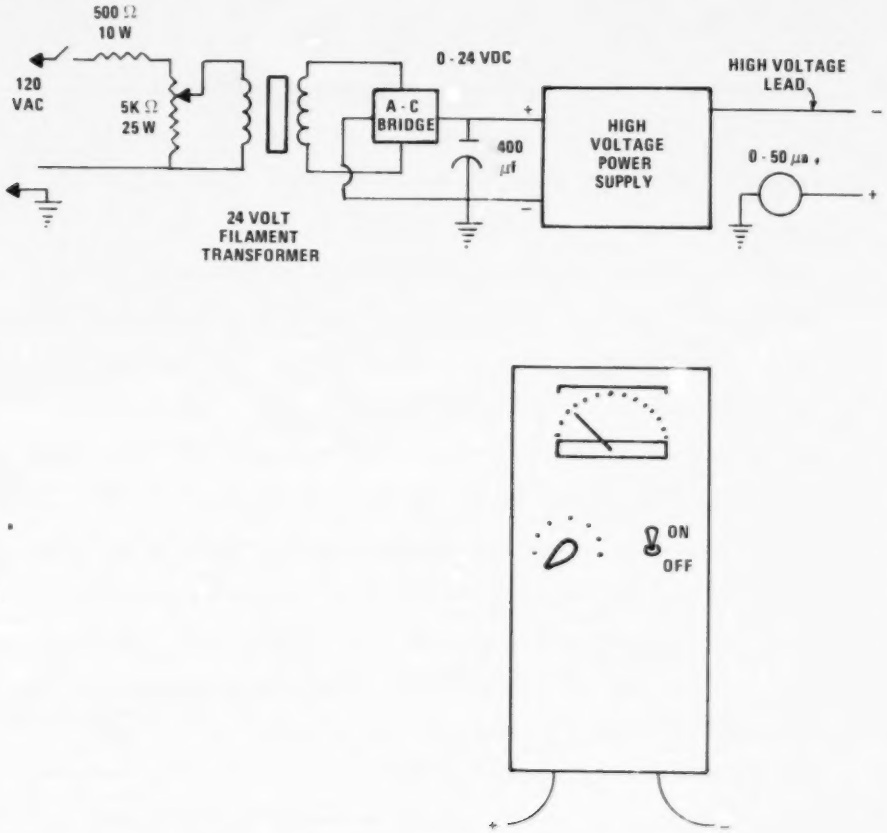

Figure 4. Power supply for electrostatic precipitator.

washed with water, and passed through the filter used for 100% IPA recovery. The 100% IPA sulfate titrated by the Barium-Thorin procedure was taken as H_2SO_4, while the sulfate recovered by the H_2O wash was taken as non-acid, water soluble sulfate.

RESULTS AND DISCUSSION

The results of the collection efficiency of ambient air particles within the size range 0.3 to 10 μm entering the ESP are shown in Figure 5. During the laboratory study, the power supply voltage was regulated to maintain the desired currents of 10, 25, and 50 μa. The curves (plotted as log vs. log) indicates that collection efficiency problems are predominant for large particles at the lower current flows. The collection efficiency at the 50 μa current was generally better than 95% for all sizes. During this laboratory study, which was performed with the ESP at room temperature, no attempt was made to establish any sulfur balance for the particles collected or lost.

Following the preliminary laboratory study, actual flue gas sampling for H_2SO_4 was conducted. During all of the routine sampling, the sequence of sampling train components was: stack to high temperature probe, ESP, filter, and acid monitor. Several series of measurements were performed involving simultaneous manual sampling for SO_2 and total sulfate while instrumentally measuring gaseous H_2SO_4. A schematic chart of one of the day's sampling results is presented in Figure 6. Several samples, some individual, others composited, were collected from the conductivity cell and titrated by the Barium-Thorin procedure. This was done to ascertain that the conductance was due solely to the collected H_2SO_4. Throughout the sampling, the greatest variable influencing the acid formation appeared to be boiler steam load (lbs/hr). As the boiler serves as a heat source for a local campus, supplemented with the steam produced by a smaller package

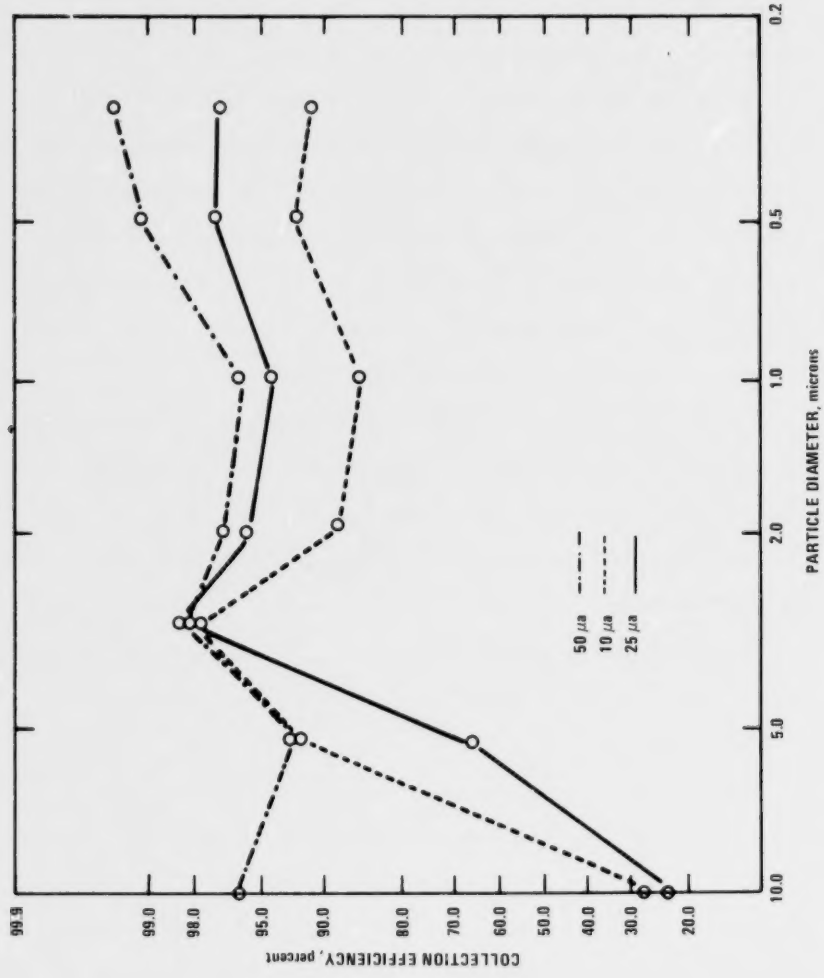

Figure 5. Collection efficiency of ESP in laboratory.

boiler, it is subject to variations of demand for short periods of time. A noticeable decrease in both TWSS and H_2SO_4 occurs in the pm. While there is less load during the pm, some of the decrease is attributed to the soot-blowing conducted at noon.

Comparison between H_2SO_4 as calculated from the conductivity measurement and the Barium-Thorin titration revealed initially higher instrument values. This was attributed to the lack of sample recovery from the conductivity cell as it empties. As the solution is blown, under pressure, from the cell, splashing and resulting sample losses occurred. As remedies were applied to avoid the losses, the instrument and titration results were in better agreement.

It can also be seen in Figure 6 the advantage of the instrumental measurements as a large number of H_2SO_4 measurements can be made during a short interval of time. Such a sequence of continual measurements could detect imbalances in boilers that integrated manual sampling would not distinguish.

For one particular series of samples, the distribution of sulfate, as water soluble or as H_2SO_4 within the probe, ESP, and filter is shown in Table 1.

The two runs shown collectively in Table 1, suggest little significant retention of H_2SO_4 by any part of the sample handling apparatus. For Run 1, nine separate H_2SO_4 measurements were made by the instruments, their average being 15.5 ppm. For Run 2, eight monitor measurements were made averaging 13.8 ppm H_2SO_4. Calculation of the per cent of the total sulfate that is measured as H_2SO_4 ((IPA recovery + moni-

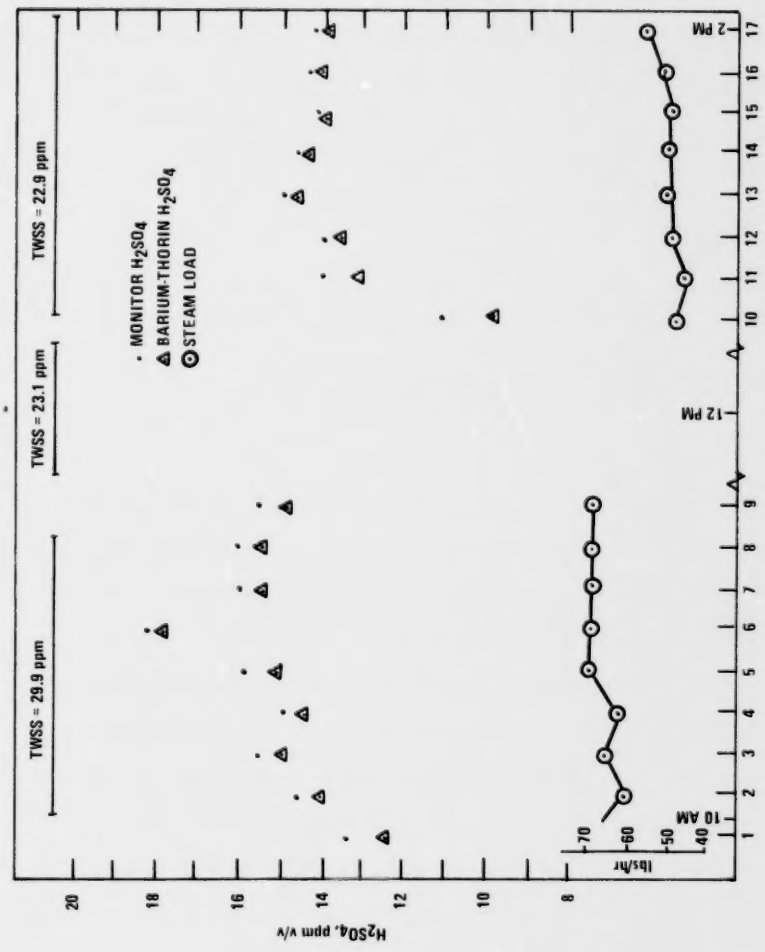

Figure 6. Comparison of data for automatic and manual acid measurements.

Table 1

DISTRIBUTION OF SULFATE IN THE SAMPLE[1] HANDLING APPARATUS

	Run No. 1		Run No. 2	
Component	IPA[2]	H_2O[2]	IPA	H_2O
Probe	0.5	0.6	<0.5	<0.5
ESP	0.5	4.6	<0.5	4.3
Filter and Holder	<0.5	<0.5	<0.5	<0.5
SAMM[3]	15.5	--	13.8	--
Total	16.5	5.2	13.8	4.3

[1]Run 1, Volume = 20.97 ft.^{3}, Run 2, Volume = 18.56 ft.^{3}
[2]Concentrations in ppm (V/V)
[3]Assumed to be H_2SO_4 from conductivity.

tor /total) X 100%) gives an acid per cent of 76.0 and 76.2%. This is not only consistent within the two tests but is in good agreement with prior manual sampling at the same boiler using similar fuel.

During the sampling that produced the Table 1 data, the probe and ESP-filter temperatures were 650 and 630°F respectively. These high temperatures had no apparent effect on enhancing an irreversible reaction between H_2SO_4 and particles, likely a result of their minimized contact time.

One prime concern of such an acid-particle separation device, was the potential for SO_2 oxidation. Such oxidation could occur by either of two means - by the high temperature catalytic conversion of SO_2 to sulfate by metal-containing particles that had accumulated in the ESP,

or by electrical discharge production of ozone (O_3) that could oxidize SO_2. In order to investigate the occurrence of either, a series of H_2SO_4 measurements was performed, which included the addition of an SO_2 gas (free of H_2SO_4) to the sample stream. After passing 27 dscf of flue gas sample through the ESP, it was disconnected from the probe, and SO_2 cylinder gas was submitted through the ESP to the monitor in the routine sampling scheme. The results of the tests are given in Table 2.

Table 2

EFFECT OF SO_2 IN ESP ON INSTRUMENT RESPONSE

Sample No.	Stack Gas / Cylinder Gas[1]	Instrument H_2SO_4 (PPM)	Volume Flue Gas dscf through ESP[2]
1	X / --	15.9	27.0
2	X / --	15.1	27.8
3	X / --	14.3	28.7
4	-- / X	2.1	28.7
5	-- / X	1.2	28.7
6	-- / X	0.8	28.7
7	-- / X	0.8	28.7
8	X / --	9.0	29.6
9	X / --	11.9	30.5
10	X / --	12.7	31.3
11	X / --	13.5	32.2

[1] 1000 ppm V/V SO_2-in-air

[2] Since sample initiation with a clean ESP and filter

While it is apparent from the data that no H_2SO_4 is being produced ultimately from the cylinder SO_2, there is a presence of acid for a few sampling cycles. As the same phenomenon had been observed prior to this study when disconnecting the ESP from the probe but when neither stack gas nor SO_2 cylinder gas was being pulled through the ESP, it was assumed that H_2SO_4 was being liberated from available surface areas. The potential for a small amount of particle-absorbed H_2SO_4 to be released is possible and would seem to be more probable than a metal surface absorption which would be irreversible. That this first possibility actually occurs is reinforced by the subsequent flue gas sampling data in Table 2, where several measurements were required after reattaching the sampling system to the stack to reestablish consistent H_2SO_4 readings. The effect of this equilibrium would be minimal upon the measurements as the amount of H_2SO_4 recovered during the No. 4 sample was 0.20 mg. Comparison of this amount to the approximate 14 to 16 mg. of H_2SO_4 at the 15 PPM concentration would give, at maximum, a 14% error. This equilibrium would have to be investigated further for flue gases with small concentrations of H_2SO_4.

CONCLUSION

Retention of particulate matter within a prototype ESP during H_2SO_4 measurements appears feasible from this study. An effort to distinguish H_2SO_4 retained by the ESP from particulate sulfate by specific solvent recovery indicated a successful separation of the

two. The ESP separation approach avoids potential enhancement of an H_2SO_4 reaction with filtered particles that can occur when using a high temperature filter.

The particle collection efficiency of the ESP was adequate enough that a quartz filter subsequent to the ESP collected negligible amounts of either H_2SO_4 or water soluble sulfates. Whether the ESP will eliminate the need of a filter for this monitoring application must be investigated further. There is a potential for non-sulfur species to be collected on the filter which in its absence would result in erroneous conductance readings by the instrument.

No attempt was made to quantify the particulate matter collected in the ESP and on the filter on a gravimetric basis. Due to the difficulty of recovering the quartz filter in weighing form, as well as the difficulty of removing particules quantitatively from the prototype ESP, the study was confined to sulfur species distribution. Design modifications currently under way should make such quantitative particle collection studies possible.

It was thought prior to actual use of the ESP that the oxidation of SO_2 would occur within it. Investigation of this indicates that introduction of SO_2 into the ESP which contains flue gas particles, and is at a high collection voltage, results in no H_2SO_4 formation.

A small, but real equilibrium between H_2SO_4 and the ESP seemed apparent during this study. It is felt that this would cause no real problems at higher H_2SO_4 ,concentrations. At lower concentrations the difficulty could be somewhat remedied if a larger sample volume was

collected, which would result in a greater amount of H_2SO_4 being collected.

A small but real error in correlation of conductivity to H_2SO_4 exists. It was felt during this study that a probable cause for the discrepancy was sample loss during recovery. The consistently low recovery of conductivity cell sulfate, even when a standardized solution of H_2SO_4 was added to the cell, (such as during calibration) seemed to confirm the source of error.

Further work must be performed to establish the maximum particle grain loading the ESP will accommodate, as well as how effectively the ESP will work for other types of combustion sources. It is felt, however, that a significant advance in gaseous H_2SO_4- particulate matter separation has been made.

ACKNOWLEDGMENTS

The authors should like to acknowledge Dean Brooks of Research Triangle Institute for constructing the ESP, and Harold Crumley at North Carolina State University for his help with the boiler.

REFERENCES

1. Corbett, P. F., Jour. Inst. Fuel, 24, 247 (1951).

2. Goksoyr, H., Ross, K., Jour. Inst. Fuel, 35, 225 (1962)

3. Cheney, J. L., Winberry, W. T., Homolya, J. B., J. Environ. Sci. and Health, A12(10), 549 (1977).

4. Ditl, P., Coughlin, W., Environ. Sci. Technol., 11, (7) 701 (1977).

5. Cheney, J. L., Homolya, J. B., Environ. Sci. Technol., to be published.

6. Cheney, J. L., Internal Report, unpublished.

7. Eaton, W. S., Strehler, D. L., EPA-600/2-76-211, July 1976.

8. Cheney, J. L., Homolya, J. B., EPA-600/9-78-020a, 53, Aug. 1978.

9. Drinker, P., J. Indust. Hyg., 14, No. 10, 364 (1932).

Received March 21, 1979
Accepted March 23, 1979